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Di(imino)pyridine Complexes as Catalysts for Homogeneous Olefin Oligomerization Reactions

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Dedicated to Professor Sultan Abu Orabi on the occasion of his 70th birthday.

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Abstract: The synthesis of bis(arylimino)pyridine complexes of seven different transition metals and their applications after activation with methylaluminoxane (MAO) in homogeneous olefin dimerization and oligomerization reactions is described. The synthesis of bis(arylimino)pyridine ligand precursors was achieved *via* condensation reactions of 2,6-diacetylpyridine with different substituted anilines. The bis(arylimino)pyridine compounds were reacted with 3d transition metal halides of the metals Ti, V, Cr, Mn, Fe, Ni and Co to give the corresponding mono-ligated complexes. Among a series of complexes with varying metal centers, but containing the same ligand, the bis(arylimino)pyridine iron(III) complex provided the best results for the dimerization of 1-hexene after activation with MAO. Beside linear products, methyl branched olefins were detected as well. For all product compositions, a marginal higher amount of hexene dimers was observed, e.g. the insertion of 1-hexene proceeds slightly faster than the insertion of 1-pentene.

Keywords: Di(imino)pyridine complexes, 3d metals, olefin oligomerization, Co-oligomerization of olefins, Structure-property relationships.

Introduction

Beside metallocene complexes^[1-4], di(imino)pyridine complexes are a promising class of catalyst precursors for dimerization and oligomerization reactions of olefins^[5-9]. Alyea and Merrell reported the first complex with nickel as central metal^[10], while Brookhart and Gibson^[11,12] recognized the catalytic potential of iron and cobalt complexes for ethylene oligomerization and polymerization after activation with methylaluminoxane (MAO). Similar as in the case of metallocene complexes^[4], di(imino)pyridine complexes show strong structure-property relationships in catalysis depending on ligand substituents and the metal^[13-18]. The activation of these catalysts with MAO is still not quite clear, but it is very likely that a catalyst cation with a metal methyl bond is formed along with an MAO counter

anion^[19-21]. Other studies suggest two different types of active species due to the fact that bimodal molecular weight distributions can be observed in certain ethylene polymerization reactions^[22,23]. The central metal can play a key role when it is changed in the series from titanium to nickel^[24-27]. It was the goal of this study to find the best metal in this type of complexes for dimerization reactions of 1-hexene with di(imino)pyridine metal catalysts.

Materials and Methods

General

All reactions were carried out under an inert gas atmosphere of pure oxygen-free argon using standard Schlenk techniques. n-Pentane, n-hexane, diethyl ether, toluene and tetrahydrofuran were purified by distillation over

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Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride, toluene over phosphorus pentoxide. Methylene chloride and carbon tetrachloride were distilled over phosphorus pentoxide. NMR spectra were recorded with Bruker ARX (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers. All spectra were recorded at 298 K. Deuterated organic solvents (CDCl_3 , CD_2Cl_2 and C_6D_6) for NMR spectroscopy were purchased from Euriso-Top and stored over molecular sieves (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rießner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited (Bergkamen). All other starting materials were commercially available and used without further purification.

Gas Chromatography/Mass Spectrometry

GC/MS spectra were recorded with a Thermo FOCUS gas chromatograph combined with a DSQ mass detector. A 30 m HP-5 fused silica column (internal diameter 0.32 mm, film 0.25 μm and flow 1 ml/min) was used and helium (4.6) was applied as carrier gas. The measurements were recorded using the following temperature program: Starting temperature 50

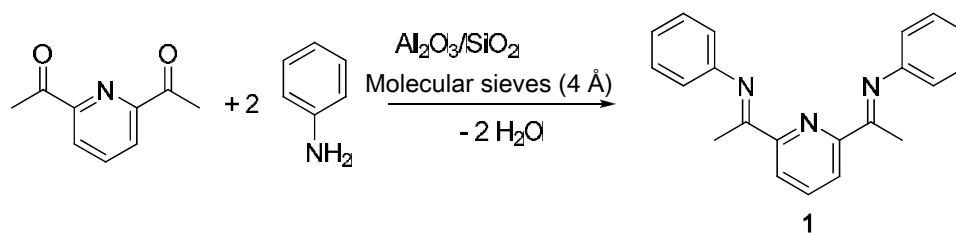
$^\circ\text{C}$, duration: 2 minutes; heating rate 20 K/min, duration: 12 minutes; final temperature 290 $^\circ\text{C}$, duration: 27 minutes.

Mass spectra were recorded with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 eV) and a VARIAN MAT 8500 spectrometer at the Zentrale Analytik of the University of Bayreuth. Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Daltonic Reflex TOF using graphite as the matrix. The laser intensity was set to 60-65%. The sample solutions were prepared in toluene or methylene chloride at a concentration of 1 mg/ml.

Results and Discussion

Synthesis and characterization of the di(imino)pyridine compound 1

Compound **1** has been described in the literature^[28] and is suitable for catalysis studies, because it would allow the coordination of different metal salts and the resulting metal complexes should not show steric hindrance for 1-hexene. The compound was synthesized according to the method reported in [29,30]:

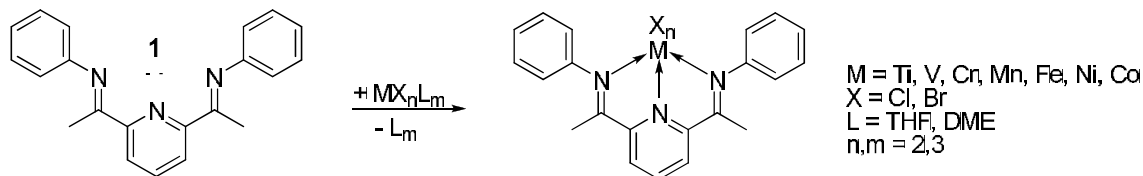


Scheme 1. Synthesis of the di(imino)pyridine compound 1.

Synthesis and characterization of the di(imino)pyridine complexes 2-8

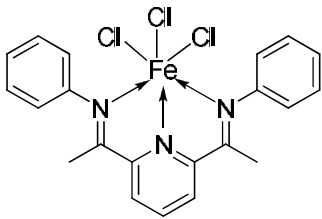
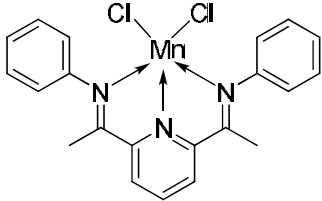
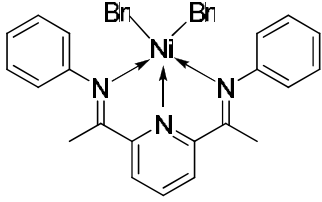
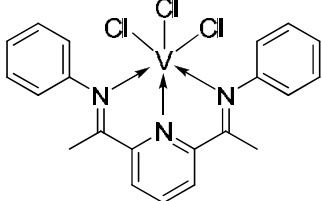
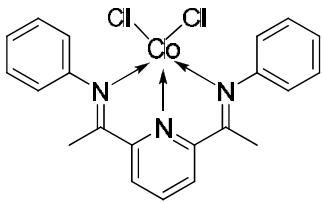
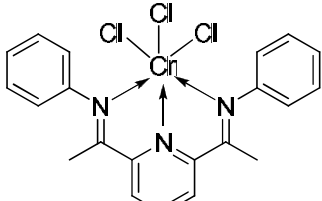
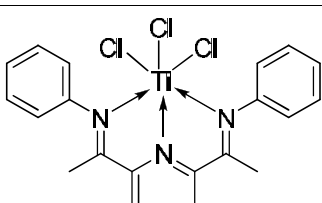
Complexes **2-8** were prepared and characterized according to literature methods, as

indicated in Table 1. The complexes are paramagnetic and do not give NMR spectra with sharp signals. Table 1 gives a survey over the synthesized complexes.



Scheme 2. General procedure for the preparation of complexes 2-8.

Table 1. Synthesized complexes.

| Nr. | Complex | Metal salt | solvent |
|-----------|---|-------------------------|-------------------|
| 2 [26] |  | FeCl ₃ | n-BuOH |
| 3 [31] |  | MnCl ₂ ·2THF | THF |
| 4 [10] |  | NiBr ₂ ·DME | THF (refluxing) |
| 5 [32] |  | VCl ₃ ·3THF | Et ₂ O |
| 6 [33] |  | CoCl ₂ | n-BuOH |
| 7 [34] |  | CrCl ₃ ·3THF | THF |
| 8 [26] |  | TiCl ₃ ·3THF | Et ₂ O |

Homogeneous dimerization of 1-hexene with complexes 2-8/MAO

Complexes **2-8** were activated with a 500-fold excess of MAO and then applied for 1-hexene oligomerization reactions for three hours at room temperature. The organic products were

characterized by GC/MS. Table 2 shows the results.

All activated complexes dimerized 1-hexene, except the manganese and cobalt derivatives. Product distributions are given in Figure 1.

Table 2. Oligomerization reactions of 1-hexene with 2-8/MAO.

| Complex | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------------------|----|----|----|---|----|----|----|
| Metal | Fe | Mn | Ni | V | Co | Cr | Ti |
| Yield[%] | 59 | - | 1 | 1 | - | 1 | 17 |
| Activity[kg/mol·h] | 29 | - | 1 | 1 | - | 1 | 4 |

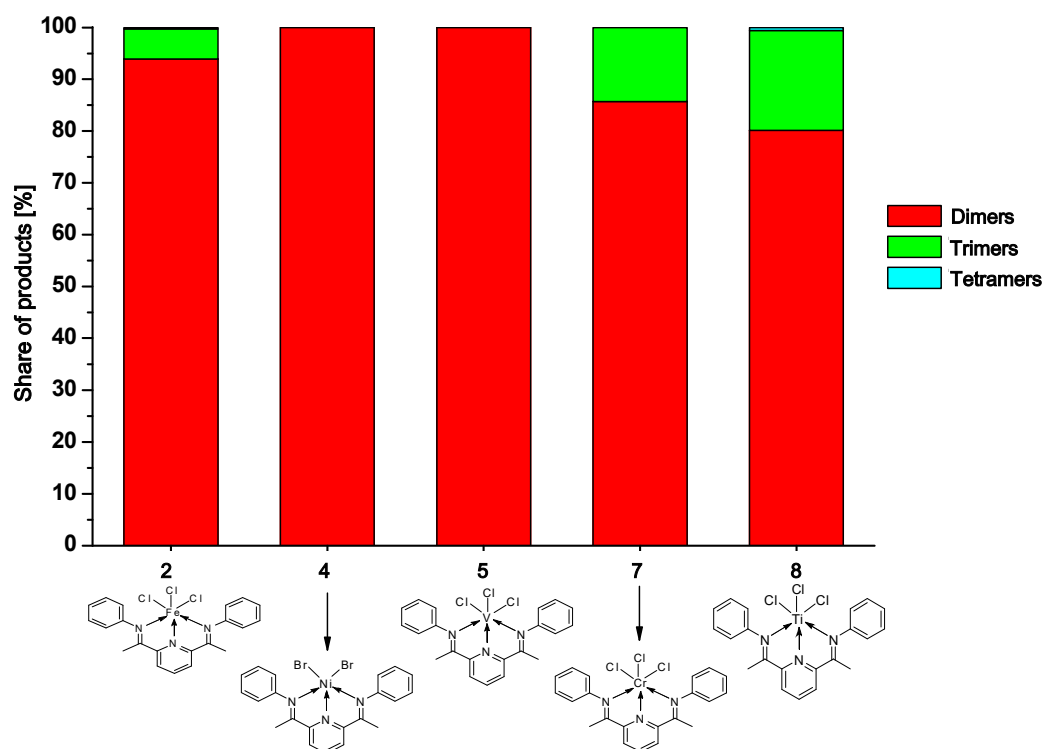


Figure 1. Product distribution from oligomerization reactions of 1-hexene with the activated complexes 2, 4, 5, 7 and 8 (M : Al = 1 : 500).

There are reports about dimerization reactions of 1-butene with the cobalt complex **6**/MAO^[26], but with very low activities (4,150 kg/mol·h). 1-Hexene could not be dimerized^[32]. The best results for 1-hexene oligomerization were obtained with the iron complex **2**/MAO (29 kg/mol·h). The titanium derivative **8** showed a comparatively low activity of 4 kg/mol·h compared with the activity of the same complex

in ethylene polymerization (5544 kg PE/mol·h)^[35]. It is obvious that the size of the olefin determines the kinetics in these reactions. The iron, chromium and titanium complexes also produced trimers, but with comparatively low yields.

Co-oligomerization reactions of 1-pentene and 1-hexene with the activated complexes 2, 4, 5, 7 and 8

Since complexes 2, 4, 5, 7 and 8 were successful in 1-hexene oligomerization reactions, the same complexes were applied as catalysts in co-oligomerization reactions of 1-pentene and 1-

hexene. The 1:1 mixtures (volumes) were oligomerized under the same conditions as described for 1-hexene. The results are given in Table 3. The results are very similar to the homo oligomerization reactions of 1-hexene. Product distributions are given in Figure 2.

Table 3. Results from co-oligomerization reactions of 1-pentene and 1-hexene with the catalysts 2, 4, 5, 7 and 8.

| Complex | Activity[kg/mol·h] | Yield[%] | Codimers[%] |
|---------|--------------------|----------|-------------|
| 2 | 23 | 81 | 45 |
| 4 | 1 | 1 | 50 |
| 5 | 1 | 4 | 56 |
| 7 | 1 | 1 | 50 |
| 8 | 1 | 3 | 45 |

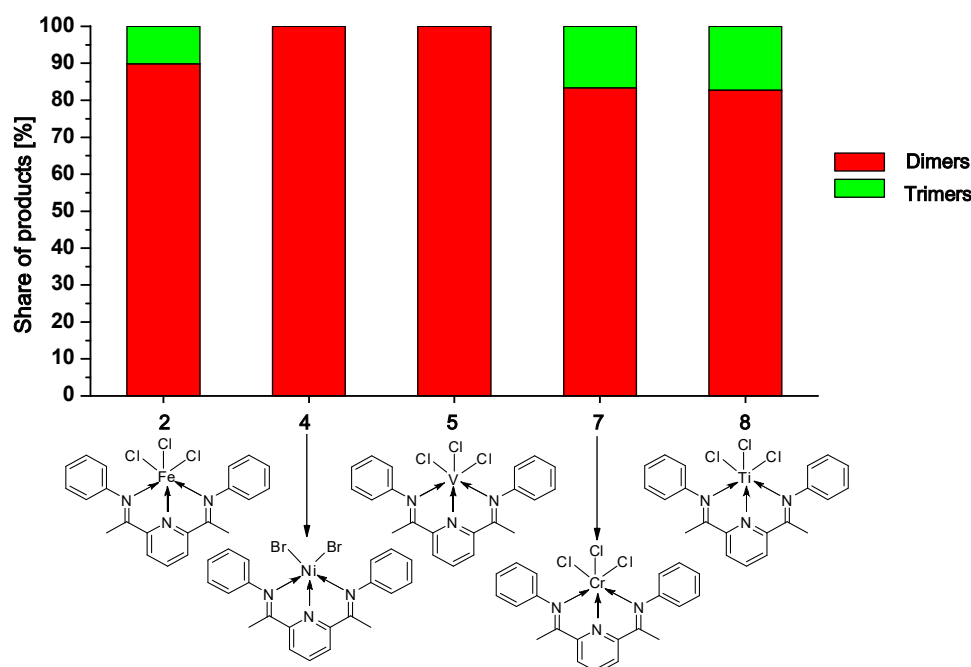


Figure 2. Product distributions for the co-oligomerization reactions of 1-pentene and 1-hexene with various catalysts.

Again, the highest activity was observed for the iron catalyst 2/MAO (23 kg/mol·h). The selectivity of dimer formation was high in all cases. Undecene, $C_{11}H_{22}$, generation was favored. This means that the combination of 1-pentene and 1-hexene is faster than the combination of the corresponding homo

monomers. The ratio of the dimers is not always 1:2:1 for $C_{10}:C_{11}:C_{12}$. Calculations show that the undecene share is the sum of decene and dodecene or even higher. The trimers have a similar composition: codimers are favored. The iron complex 2/MAO produced a 1:2:2:2 ratio of $C_{15}:C_{16}:C_{17}:C_{18}$ olefins. The titanium catalyst

8/MAO delivered a 1:1:2:1 ration of trimers, indicating that 1-hexene incorporation is favored.

Conclusions

Di(imino)pyridine complexes with 3d metals in the oxidation states II (Mn, Co, Ni) and III (Ti, V, Cr, Fe) can be activated with MAO and applied as catalyst precursors for oligomerization reactions of higher olefins, like 1-pentene and 1-hexene. The central metal plays a key role for

the performance of such catalysts as one and the same ligand was applied in these reactions. Obviously, the central metal determines the kinetics of various reaction steps in the course of these reactions, like olefin coordination, olefin insertion and chain termination.

Acknowledgements

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References

- [1] Kaminsky, W.; Fernandes, M., *Polyolefins Journal*, **2015**, 2, 1.
- [2] Redshaw, C.; Tang, Y., *Chem. Soc. Rev.*, **2012**, 41, 4484.
- [3] Baier, M.C.; Zuideveld, M.A.; Mecking, S., *Angew. Chem. Int. Ed.*, **2014**, 53, 97
- [4] Alt, H.G.; Köppl, A., *Chem. Rev.*, **2000**, 100, 1205.
- [5] Ritter, T.H.; Alt, H.G., *Polyolefins J.*, **2020**, 7, 79 in press.
- [6] Sauter, D.W.; Taoufik, M.; Boisson, C., *Polymers*, **2017**, 9, 185.
- [7] Zhang, R.; Han, M.; Ma, Y.; Solan, G.A.; Liang, T.; Sun, W.-H., *Dalton Trans.*, **2019**, 48, 17488.
- [8] Flisak, Z.; Sun, W.-H., *ACS Catal.*, **2015**, 5, 4713.
- [9] Chirik, P.J., *Angew. Chem. Int. Ed. Engl.*, **2017**, 56, 5170.
- [10] Alyea, E.C.; Merrell, P.H., *Syn. React. Inorg. Metal-Org. Chem.*, **1974**, 4, 535.
- [11] Small, B.L.; M. Brookhart, M; Bennett, A.M.A., *J. Am. Chem. Soc.*, **1998**, 120, 4049.
- [12] Britovsek, G.J.P.; Gibson, V.C.; Kimberley, B.S.; Maddox, P. J.; McTravish, S. J., Solan, G.A.; White, A.J.P.; Williams, B. S., *Chem. Commun.*, **1998**, 849.
- [13] Schmidt, R.; Welch, M.B.; Palackal, S.J.; Alt, H.G., *J. Mol. Cat., A: Chem.*, **2002**, 179, 155.
- [14] Britovsek, G.J.P.; Gibson, V.C.; Hoarau, O.D.; Spitzmesser, S.K.; White, A.J.P.; Williams, D.J., *Inorg. Chem.*, **2003**, 42, 3454.
- [15] Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G.P.A.; Budzelaar, P.H.M., *J. Am. Chem. Soc.*, **2002**, 124, 12268.
- [16] Gibson, V.C.; Redshaw, C.; Solan, G.A., *Chem. Rev.*, **2007**, 107, 1745.
- [17] Smit, T.M.; Tomov, A.K.; Gibson, V.C.; White, A.J.P.; Williams, D.J., *Inorg. Chem.*, **2004**, 43, 6511.
- [18] Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P.H.M., *Dalt. Trans.*, **2006**, 5542.
- [19] Talsi, E.P.; Babushkin, D.E.; Semikolenova, N.V.; Zudin, V.N.; Panchenko, V.N.; Zakharov, V.A., *Macromol. Chem. Phys.*, **2001**, 202, 2046.
- [20] Bryliakov, K.P.; Talsi, E.P.; Semikolenova, N.V.; Zakharov, V.A., *Organomet.*, **2009**, 28, 3225.
- [21] Schmidt, R.; Das, P. K.; Welch, M. B.; Knudsen, R.D., *J. Mol. Cat.; A: Chem.*, **2004**, 222, 27.
- [22] Barabanov, A.A.; V. A. Zakharov; N. V. Semikolenova; L. G. Echevskaja; M. A. Matsko, *Macromol. Chem. Phys.*, **2005**, 206, 2292.
- [23] Barabanov, A.A.; Bukatov, G.D.; Zakharov, V.A.; Semikolenova, N.V.; Mikenas, T.B.; Echevskaja, L.G.; Matsko, M.A., *Macromol. Chem. Phys.*, **2006**, 207, 1368.
- [24] Su, B., Feng, G., *Polym. Int.*, **2010**, 59, 1058.
- [25] Seitz, M.; Görl, C.; Milius, W.; Alt, H.G., *Jordan J. Chem.*, **2008**, 3, 109.

- [26] Calderazzo, F.; Englert, U.; Pampaloni, G.; Santi, R.; Sommazzi, A.; Zinna, M., *Dalton Trans.*, **2005**, 914.
- [27] Gong, D.; Wang, B.; Bai, C.; Bi, J., Wang, F.; Dong, W.; Zhang, X.; Jiang, L., *Polymer*, **2009**, 50, 6259.
- [28] Abu-Surrah, A.S.; Lappalainen, K.; Piironen, U.; Lehmus, P.; Repo, T., Leskelä, M., *J. Organomet. Chem.*, **2002**, 648, 55.
- [29] Zhang, Z.; Chen, S.; Zhang, X.; Li, H., Ke, Y., Lu, Y., Hu, Y., *J. Mol. Cat. A: Chem.*, **2005**, 230, 1.
- [30] Chen, Y., Qian, C., Sun, J., *Organometallics*, **2003**, 22, 1231.
- [31] Edwards, D.A.; Mahon, M.F.; Martin, W.R.; Molloy, K. C.; Fanwick, P. E.; Walton, R. A., *J. Chem. Soc. Dalton Trans.*, **1990**, 3161.
- [32] Schmidt, R.; Welch, M. B.; Knudsen, R.D.; Gottfried, S.; Alt, H.G., *J. Mol. Cat. A: Chem.*, **2004**, 222, 9.
- [33] Edwards, D.A.; Edwards, S.D.; Martin, W.R., Pringle, T.J.; Thornton, P., *Polyhedron*, **1992**, 11, 1569.
- [34] Nakayaa, Y.; Sogo, K.; Yasuda, H.; Shiono, T., *J. Polym Sci.; A: Polym. Chem.*, **2005**, 43, 3368.